

In situ μ^+ SR measurements on the hydrogen desorption reaction of magnesium hydride

I Umegaki^{1*}, H Nozaki¹, M Harada¹, Y Higuchi¹, T Noritake¹,
M Matsumoto¹, S-i Towata¹, E J Ansaldo², J H Brewer^{2,3}, A Koda⁴,
Y Miyake⁴ and J Sugiyama^{1**}

¹ Toyota Central Research & Development Laboratories, Inc., 41-1 Yokomichi, Nagakute, Aichi 480-1192, Japan

² TRIUMF, 4004 Wesbrook Mall, Vancouver, BC, V6T 2A3 Canada

³ Department of Physics & Astronomy, University of British Columbia, Vancouver, BC, V6T 1Z1 Canada

⁴ Muon Science Laboratory, Institute of Materials Structure Science, KEK, Tsukuba, Ibaraki 305-0801, Japan

E-mail: *e4774@mosk.tytlabs.co.jp, **e0589@mosk.tytlabs.co.jp

Abstract. In order to clarify the reason why the hydrogen desorption temperature (T_d) of MgH_2 is lowered by milling, we have studied the change in a local nuclear magnetic field with temperature by means of μ^+ SR. We have found a very clear oscillation in the ZF-spectrum at 2 K for the “milled” and “milled with Nb_2O_5 ” samples, while such oscillation is weaker for the “as prepared” MgH_2 . It was also found that the oscillation signal is stable up to 250 K and is assigned mainly due to the formation of a H- μ -H system. At temperatures above ambient T , we also found that the ZF- μ^+ SR spectrum exhibits a static Kubo-Toyabe behavior due to the nuclear magnetic field of ^1H . Furthermore, it was clarified that rapid H diffusion starts well below T_d only in the milled samples, leading to the conclusion that the consequent enhanced diffusion rate in MgH_2 is essential to accelerate the desorption reaction and to decrease T_d .

1. Introduction

Despite huge efforts for searching and developing hydrogen storage materials [1], it is still a great challenge for materials science and engineering to make a safe, light-weight, high-capacity hydrogen storage system. Unfortunately, all the alloys are too heavy to carry on automobiles due to their small gravimetric H_2 density. On the other hand, complex hydrides are possible candidates for future onboard hydrogen storage materials [2, 3], if their hydrogen desorption temperature (T_d) is reasonably lowered, ideally down to ambient temperature [4, 5]. Among many complex hydrides, magnesium hydride, MgH_2 (Fig. 1), has attracted special attention due to its relatively large gravimetric H_2 density. Furthermore, since T_d is decreased down to 500 K by milling MgH_2 with 5 wt% Nb_2O_5 [6], for reasons currently unknown [7, 8], MgH_2 is considered to be one of the most promising hydrogen storage materials.

Recent μ^+ SR experiments on the other complex-type hydrides, NaAlH_4 [9] and $M(\text{BH}_4)_n$ [10], proposed a significant role of H-diffusion in solids on determining T_d through the observation of H- μ -H and/or H- μ systems. This is a promising future of μ^+ SR, because such three-spin and two-spin systems are formed only when muons are implanted into samples. However,



the oscillation signals due to the formation of such systems become weaker and weaker with increasing temperature. As a result, there was no μ^+ SR study of such compounds above ambient temperature. Even if the implanted muons are mobile by thermal activation, muons are still expected to *see* local nuclear magnetic fields via a dynamic Kubo-Toyabe behavior. We have, therefore, measured μ^+ SR spectra on MgH_2 in a wide temperature range in order to investigate the mechanism on the decrease in T_d by milling with Nb_2O_5 .

2. Experiment

A coarse MgH_2 powder, which is called as an “as prepared” sample, was purchased from Avocado. The average grain diameter (d_g) of the “as prepared” sample is 100 nm. Then, the “as prepared” sample was packed in a ball mill container in an Ar-filled glove-box, and then, milled for 24 hours by a planetary ball mill in an Ar atmosphere in order to reduce d_g down to 8-9 nm (a “milled” sample). Using the same milling procedure, but together with 5 wt% Nb_2O_5 powder, a “milled with Nb_2O_5 ” sample was also prepared. T_d of the three samples was determined by temperature-programmed desorption (TPD) measurements, in which the desorption gas was detected by a mass spectrometer (TP-5000, Ohkura-Riken) during heating with a rate 5 K/min in a He flow with a flow rate 60 ml/min. Such measurements revealed that the amount of desorbed hydrogen does not change with milling.

For the μ^+ SR measurements, each powder sample was pressed into a pellet, and then, the pellet was packed into a titanium cell sealed with a gold O-ring in a glovebox, because MgH_2 is sensitive to moisture. The μ^+ SR spectra were measured at TRIUMF in the temperature range between 2 and 300 K, and at J-PARC in the temperature range between 300 and 750 K. Particularly in J-PARC, the pressure of the sample space, which is evacuated by a turbo-molecular pump, was monitored during the μ^+ SR measurements. In order to release H_2 in the Ti cell to the sample space, small holes were made on the Ti foil window just before the measurements.

3. Results

Figure 2 shows the TPD profile of the present three samples. It is confirmed that $T_d = 710$ K for the “as prepared” sample, but $T_d = 620$ K for the “milled” sample and 530 K for the “milled

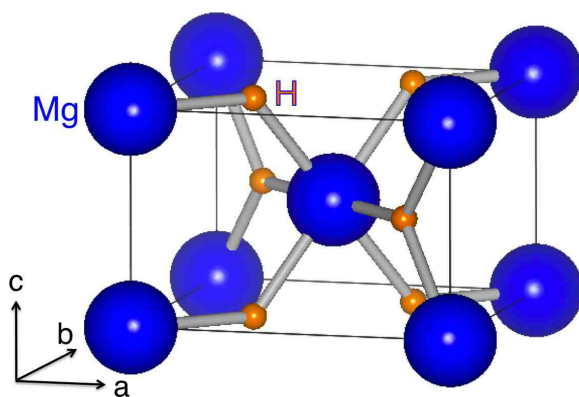


Figure 1. Crystal structure of tetragonal MgH_2 with space group $P4_2/mnm$, $a = 4.5180$ Å and $c = 3.0211$ Å. Mg ion occupies the center and corner sites in a unit cell, and H ions are connected to Mg ions with the bond length 1.95 Å[11].

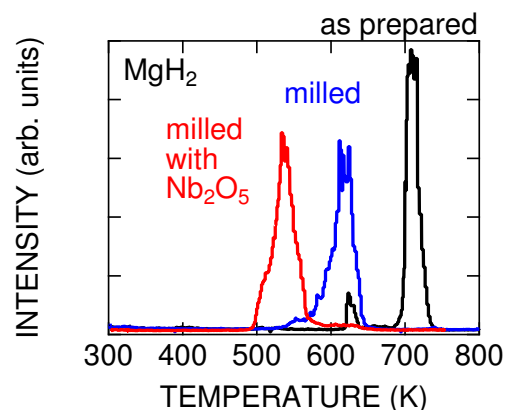


Figure 2. Temperature-programmed desorption (TPD) profile for the “as prepared”, “milled”, and “milled with Nb_2O_5 ” MgH_2 samples.

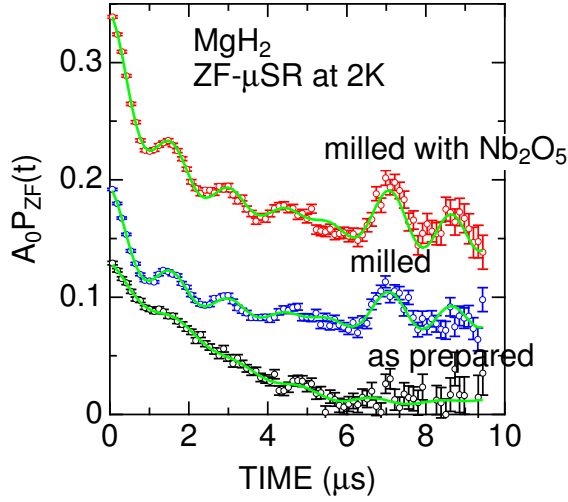


Figure 3. ZF- μ^+ SR spectra for the three kinds of MgH₂ measured at 2 K in TRIUMF. The spectra for the “milled” and “milled with Nb₂O₅” samples are shifted upward by 0.05 and 0.1 for clarity of display. The oscillations indicate the formation of the H- μ -H system.

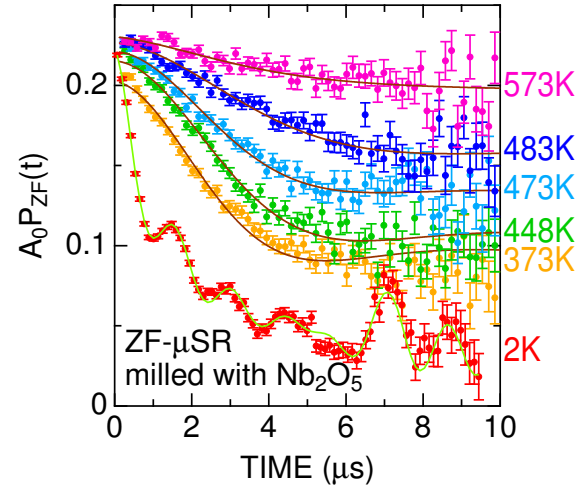


Figure 4. Temperature variation of ZF- μ^+ SR spectrum for the “milled with Nb₂O₅” sample obtained in J-PARC. The data at 2 K, which is the same to that in Fig. 3, is also plotted for comparison, but shifted downward by 0.05 for clarity of display.

with Nb₂O₅” sample.

3.1. Below ambient temperature

Figure 3 shows the ZF- μ^+ SR spectra obtained at 2 K for the three samples. The ZF-spectra for the two milled samples exhibit a very clear oscillation, indicating the formation of the H- μ -H and/or H- μ systems. In fact, the ZF-spectra for both samples were reasonably fitted by a combination of an exponentially relaxing H- μ -H signal, two exponentially relaxing cosine signals probably due to a localized state with three (or more) spins, and two non-oscillatory relaxing signals. The other four signals besides the H- μ -H signal suggest the presence of multiple muon sites in the MgH₂ lattice. We will call this complex situation as the formation of a “H- μ -H like” system.

Back to the H- μ -H signal, the muon-spin polarization function ($P_{H\mu H}$) is given by [12];

$$\begin{aligned} P_{H\mu H}(t) = & \frac{1}{2} + \frac{1}{6} \cos(\sqrt{3}\omega_d t) \\ & + \frac{1 + 1/\sqrt{3}}{6} \cos\left(\frac{3 + \sqrt{3}}{2}\omega_d t\right) \\ & + \frac{1 - 1/\sqrt{3}}{6} \cos\left(\frac{3 - \sqrt{3}}{2}\omega_d t\right), \end{aligned} \quad (1)$$

and [12, 13]

$$\omega_d \equiv 2\pi f_d = \frac{\mu_0 \hbar \gamma_\mu \gamma_H}{4\pi r^3}. \quad (2)$$

Here, γ_μ is the nuclear gyromagnetic ratio of μ , γ_H is the nuclear gyromagnetic ratio of ^1H , and r is the distance between μ and H in the H- μ -H system. Since the fit provided that $f_d = 0.25$ MHz

for both “milled sample” and “milled with Nb₂O₅” samples, r is estimated as 1.16 Å, which is close to a half of the distance between the two nearest neighboring hydrogens (2.52 Å). This means that some of the implanted muons (about 25%) sit at the middle of the two neighboring hydrogens, resulting in the formation of a H- μ -H system.

Note that even for the “as prepared” sample, the ZF-spectrum shows a weaker, but clearly evident oscillation. Therefore, the formation of the H- μ -H like system is found to be an intrinsic phenomenon for MgH₂. The enhancement of the oscillatory signal by milling suggests the role of fresh surface on the formation of the H- μ -H like system. That is, for the “as prepared” sample, hydrogens in the surface layer are expected to bind to oxygens, while it is stored in Ar atmosphere. As a result, the H- μ -H like signal is a minor component in the ZF-spectrum for the “as prepared” sample, together due to the large particle size of the sample (100 nm). This also proposes a significant role of surface to determine T_d for MgH₂.

In brief summary, although the μ^+ SR experiment at low temperatures clarified the variation of static nature of MgH₂ by milling, there is still no information on dynamics of hydrogens. We therefore measured μ^+ SR spectra for the three samples at high temperatures, i.e. from ambient temperature to T_d and above.

3.2. Above ambient temperature

Figure 4 shows the ZF- μ^+ SR spectra at high temperatures for the “milled with Nb₂O₅” sample. At 373 K, the ZF-spectrum exhibits a static Gaussian Kubo-Toyabe (KT) behavior due to a nuclear magnetic field of ¹H. As temperature increases from 373 K, the KT relaxation becomes weaker and weaker, and finally, the spectrum looks almost time-independent at 573 K.

In order to know the change in the μ^+ SR parameters with temperature, Figs. 5(b), 5(c) and 5(d) show the temperature dependences of the relaxation rate (λ_{TF}) of the wTF-spectrum, which corresponds to a spin-spin relaxation rate ($1/T_2$), i.e., the distribution width of the nuclear magnetic field (Δ), and the field fluctuation rate (ν) for the three samples. For the “as prepared sample”, λ_{TF} , Δ and ν are almost temperature independent up to 630 K, and then become very small, eventually zero at temperatures above T_d . This means that the hydrogen desorption reaction abruptly occurs and completes at T_d . In fact, at temperatures above T_d , the wTF-spectrum exhibited a non-relaxing oscillatory signal from the Ti-cell and Mg. Furthermore, the wTF-spectrum obtained in cooling mode from 750 K did not change even below T_d , suggesting that all the hydrogen atoms are removed from the sample. For such situation, since the ZF-spectrum exhibits an exponentially relaxing behavior with a very small relaxation rate, it is impossible to evaluate Δ and ν . This is the reason why we show the $\lambda_{TF}(T)$ curve in Fig. 5.

For the “milled” sample, λ_{TF} gradually decreases with temperature above 470 K, while ν apparently increases with temperature also above 470 K. This suggests that the H-desorption reaction starts to occur far below T_d (=620 K) for the “milled” sample, because $1/T_2$ decreases with decreasing the number density of H around the muon. Moreover, the increase in ν implies rapid diffusion of H and/or muon in the sample, which is proposed to be a significant factor to decrease T_d for the other hydrogen storage materials, such as LiAlH₄ [9] and $M(\text{BH}_4)_n$ [10].

For the “milled with Nb₂O₅” sample, as temperature increases from ambient temperature, ν starts to increase above 450 K as for the “milled” sample, but the slope ($d\nu/dT$) is rather steep compared with that for the “milled” sample and ν reaches a maximum ($\sim 0.5 \times 10^6 \text{ s}^{-1}$) at 550 K. The maximum value of ν is larger by 2.5 times than the highest ν for the “milled” sample. Simultaneously, the $\lambda_{TF}(T)$ curve shows a rapid decrease down to zero at around 500 K. These changes are good agreement with the TPD curve [Fig. 5(a)]. It should be emphasized that, even for the “milled” sample, ν also starts to increase above 470 K. In addition, we measured the wTF-spectra for the “milled with Nb₂O₅” sample with decreasing T above T_d . Since the wTF-spectrum does not exhibit a relaxation even below T_d due to the absence of H, λ_{TF} measured on cooling is almost zero down to the lowest T measured (=433 K) [Fig. 5(b)].

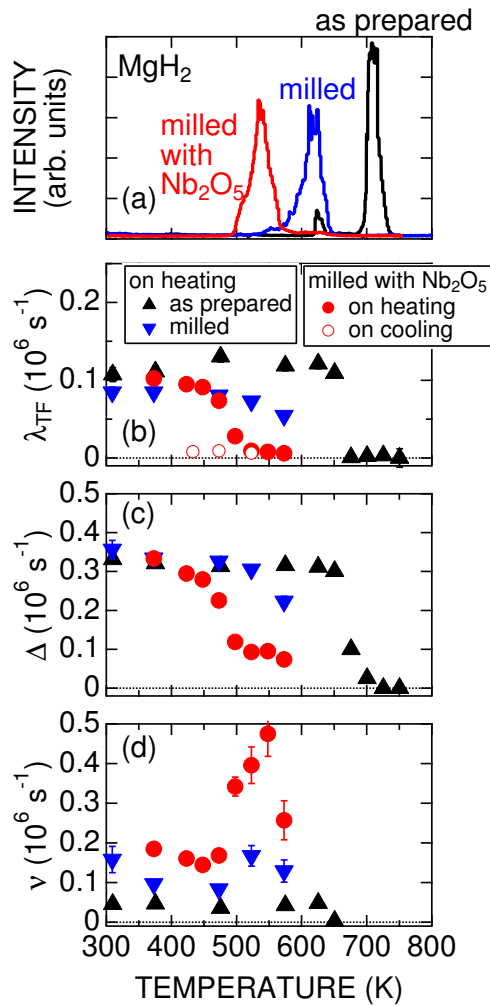


Figure 5. (a) TPD result and temperature dependences of (b) the exponential relaxation rate of the weak transverse field spectrum (λ_{TF}) and (c) the filed distribution width (Δ) (d) the filed fluctuation rate (ν) for the “as prepared”, “milled”, and “milled with Nb₂O₅” samples. (a) is the same to Fig. 2.

After the measurements above T_d , the residue in the Ti cell was checked by XRD analyses in air. It was found that the residue consists of mainly Mg and small amount of MgO, Mg(OH)₂, and MgH₂ (below 3%). This means that almost all the hydrogen were released from the sample by the hydrogen desorption reaction.

4. Discussion

Here, we discuss the relationship between the magnitude of T_d and the obtained μ^+ SR parameters. The most remarkable difference of the μ^+ SR parameters among the three samples is that ν starts to increase above 470 K both for the “milled” and “milled with Nb₂O₅” samples, but DOES NOT even at T_d for the “as prepared” sample. The increase in ν is naturally caused

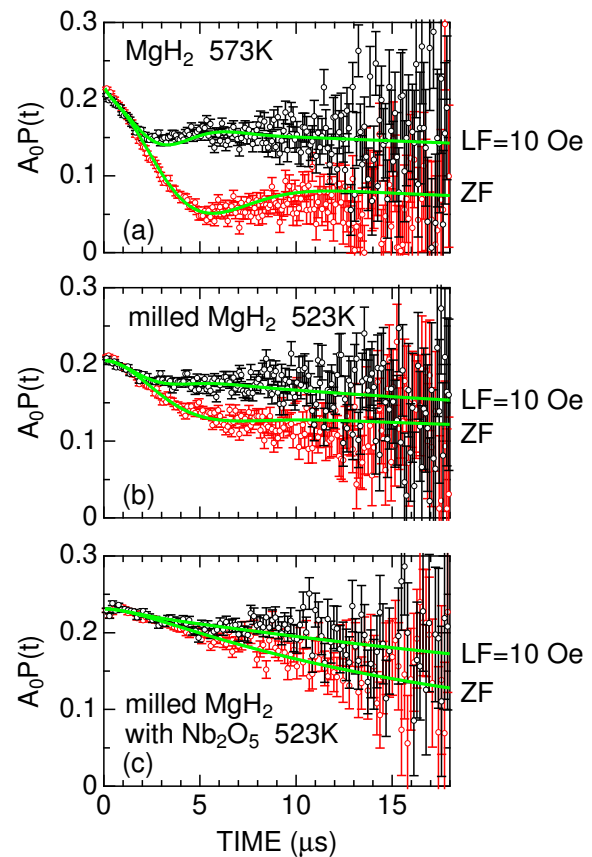


Figure 6. ZF- and LF-spectra for (a) the “as prepared” sample at 573 K, (b) the “milled” sample at 523 K, and (c) the “milled with Nb₂O₅” sample. The applied LF was 10 Oe. These spectra were obtained in J-PARC.

by H- and/or μ -diffusion in the MgH_2 lattice. Furthermore, since μ is static even at 573 K in the “as prepared” sample (Fig. 6), the increase in ν (decrease in λ_{TF}) is likely due to H-diffusion, which also induces μ -diffusion. Then, why H- and μ -diffusion are observed only for the two milled samples? As mentioned in Sec. 3.1, each particle in the two milled samples is surrounded by fresh surface with greater surface area to particle volume ratio, across which the liberated hydrogen is released to atmosphere. The fresh surface, which is evidenced by the presence of the H- μ -H like system, is naturally thought as a starting point of the hydrogen desorption reaction, meaning the formation of defects at the surface. When such defects are formed at the surface, the liberated hydrogen is easily moved to the surface through H-diffusion in solids. This would be a reason for the decrease in T_d by milling. Since the milling with Nb_2O_5 does not change the onset temperature of the hydrogen desorption reaction, Nb_2O_5 is most likely to function as catalyst, leading to the enhancement of the reaction rate.

Finally, we wish to mention the tentative result of an in situ μ^+ SR measurement. During the μ^+ SR measurement on the “milled with Nb_2O_5 ” sample, we also monitored the pressure (P) in the sample space. When P starts to increase due to the hydrogen desorption reaction, λ_{TF} starts to decrease, whereas ν starts to increase. This is, to our knowledge, a first “**in situ μ^+ SR measurement**” to see the change in real time local magnetic environments. Such in situ measurements will provide significant information on the desorption reaction in hydrogen storage materials.

Acknowledgments

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